

Computing Equilibrium Lattice Constant

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1 Reading a Log File

In the example scripts of Manual 02, the command `setnolog` was activated and the simulation results were printed out to the standard output, which is usually your terminal screen. If you want to keep the record of this information, you can comment out the `setnolog` command by adding `#` in front of it. This will create a log file `A.log` in the directory specified by `dirname`. For example, if you run `mo.script` in Manual 02 but with `setnolog` commented out, then you will find the `A.log` file in the `runs/mo-example` directory. To read this file, type

```
$ more runs/mo-example/A.log
```

You will see the same content as you previously saw on screen. In the log file, the lines starting with “ASSIGN” show that certain variables parameters are assigned to the values as specified in the script file. The lines with “EXEC” show the execution of certain commands. After the `eval` command is executed, properties such as number of atoms (`_NP`), potential energy (`EPOT`), kinetic energy (`KATOM`), pressure (`PRESSURE`) and stress (`Stress`) are also printed. At the end of the simulation, the log file may be zipped as “`A.log.gz`”, in which case you can use

```
$ gzip -cd runs/mo-example/A.log.gz | more
```

to see the content. To search for a specific content (e.g. `EPOT`) in the log file, you may use

```
$ grep EPOT runs/mo-example/A.log
```

or

```
$ gzip -cd runs/mo-example/A.log.gz | grep EPOT
```

depending on whether the log file is zipped. In case you want to “grep” several

lines before and after your keyword (e.g. Stress), you can use

```
$ grep -3 Stress runs/mo-example/A.log
```

This will show three lines above and below any line containing the keyword “Stress”.

2 Equilibrium Lattice Constant and Cohesive Energy

Under ambient condition Silicon takes the the diamond-cubic (DC) structure. But in a computer simulation, we can create Si crystals with different hypothetical structures, such as face-centered-cubic (FCC), body-centered-cubic (BCC), or simple-cubic (SC). A good potential model should be able to tell us that the DC structure is the one with the lowest energy, hence it is the most favorable structure for Silicon. In this section, we will perform such calculations using MD++.

Let us define the lattice energy Φ and the number density ρ as

$$\begin{aligned}\Phi &= \frac{E_{pot}}{N} \\ \rho &= \frac{N}{V}\end{aligned}$$

where E_{pot} is the potential energy of the crystal, N is total number of atoms in the simulation cell (corresponding to variable `_NP` in MD++) and V is the volume of the simulation cell. Run MD++ with following command line to use the Stillinger-Weber (SW) potential model [1, 2].

```
$ bin/sw_gpp scripts/ME346/si_polytype.script
```

Here is the content of the `si_polytype.script`.

```
# --shell-script--
#setnolog
setoverwrite
dirname = runs/si_polytype

#-----
#Create Perfect Lattice Configuration
#
crystalstructure = diamond-cubic
latticeconst = 5.4309529817532409 #(A) for Si
latticesize = [ 1 0 0 3
                0 1 0 3
```

```

                                0 0 1 3 ]
makecrystal eval

latticeconst = 4.850 makecrystal eval
latticeconst = 4.950 makecrystal eval
latticeconst = 5.050 makecrystal eval
:
(many lines omitted here for brevity)
:
latticeconst = 5.900 makecrystal eval
latticeconst = 6.000 makecrystal eval
latticeconst = 6.100 makecrystal eval

crystalstructure = face-centered-cubic

latticeconst = 4.105 makecrystal eval
latticeconst = 4.110 makecrystal eval
:
:
latticeconst = 4.205 makecrystal eval
latticeconst = 4.215 makecrystal eval

crystalstructure = body-centered-cubic

latticeconst = 3.210 makecrystal eval
latticeconst = 3.220 makecrystal eval
:
:
latticeconst = 3.320 makecrystal eval
latticeconst = 3.340 makecrystal eval

crystalstructure = simple-cubic

latticeconst = 2.550 makecrystal eval
latticeconst = 2.600 makecrystal eval
:
:
latticeconst = 2.640 makecrystal eval
latticeconst = 2.650 makecrystal eval
quit

```

From the log file, you can find number of atoms $_NP$ for the $3 \times 3 \times 3$ DC cell

to be 216. This number can also be obtained by calculating $8 \times 3^3 = 216$, since there are eight atoms in the DC unit cell. For other crystal structures, the number of atoms in the $3 \times 3 \times 3$ cell is given in the following table.

Crystal Structure	No. of atoms in the unit cell	Total No. of atoms
SC	1	27
BCC	2	54
FCC	4	108
DC	8	216

The potential energy at each different lattice constant can also be read from the log file by typing

```
$ grep EPOT runs/si_polytype/A.log
```

The volume of a simulation cell V can be obtained from the determinant of the matrix \mathbf{H} .¹ When \mathbf{H} is a diagonal matrix (the same is true for an upper triangular matrix),

$$V = \det(\mathbf{H}) = H(1, 1) H(2, 2) H(3, 3)$$

the volume is the product of the entries in the main diagonal of \mathbf{H} . The unit of length in MD++ is Å and the unit of volume is Å³. From these, we can calculate the lattice energy Φ (in eV) of Silicon as a function of the number density ρ (in $1/\text{Å}^3$), for different crystal structures, as shown in Fig.1(a) and Fig.1(b). The structure with the lowest energy is DC. The equilibrium lattice constant a_0 corresponds to the number density that gives the minimum of the $\Phi(\rho)$ curve. The minimum of Φ is also called the cohesive energy E_{coh} . For DC Silicon, $a_0 = 5.431\text{Å}$ and $E_{\text{coh}} = -4.63$ eV.

3 Bulk Modulus

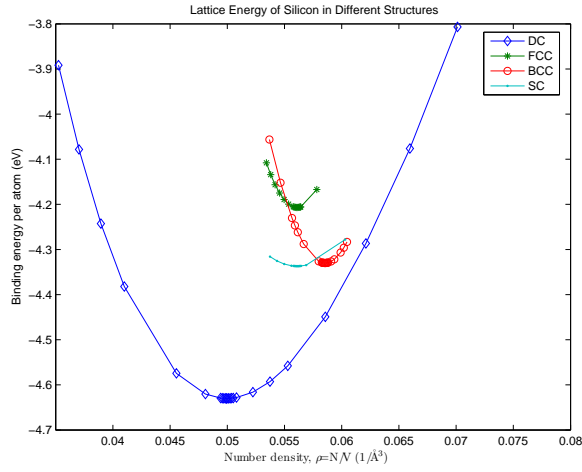
The curvature of the $\Phi(\rho)$ curve near the minimum also tells us the bulk modulus of the crystal. The bulk modulus B is defined as ²

$$B = V \frac{\partial^2 \Phi}{\partial V^2} \Big|_{V=V_0} \quad (1)$$

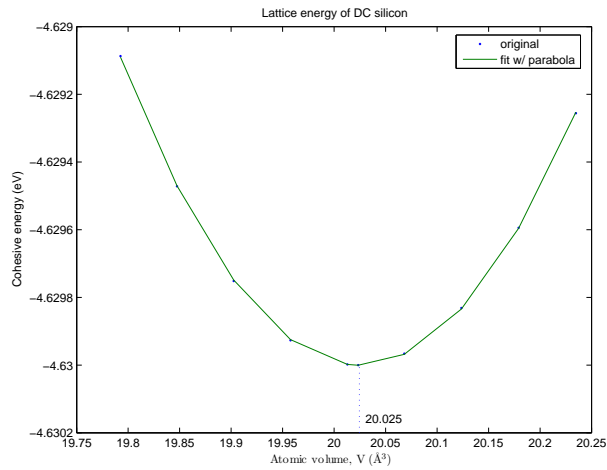
where V_0 is the equilibrium atomic volume (corresponding to the energy minimum). To compute the second derivative, plot Φ as a function of $V = 1/\rho$ and fit the $\Phi(V)$ curve in the neighborhood of the minimum by a quadratic function, i.e. $\Phi = c_0 + c_1 V + c_2 V^2$, as shown in Fig.1(b). This can be done by the Matlab

¹The matrix \mathbf{H} defines size and shape of the simulation cell. $\mathbf{H} = [\mathbf{c}_1 \ \mathbf{c}_2 \ \mathbf{c}_3]$ where \mathbf{c}_i 's are three periodicity vectors. In MD++, the matrix \mathbf{H} becomes a diagonal matrix when the supercell is a rectangular box (after reorienting the coordinate system with the repeat vectors).

²This is because $B = -V\partial P/\partial V$ and $P = -\partial\Phi/\partial V$.



(a) Si in different crystal structures



(b) Lattice energy of Si DC

Figure 1: (a) The lattice energy of silicon for four different crystal structures (DC, FCC, BCC, and SC) are plotted as number density. Silicon has the lowest energy in the diamond cubic structure. (b) The lattice energy of DC silicon as a function of the atomic volume is fitted with a parabola (dash-dot line) and with spline interpolation (solid line).

command `polyfit` and the result is $c_2 = 0.0169$ (in unit of $\text{eV}/\text{\AA}^6$). Evaluating Eq. (1) with ($V_0 = 20.025\text{\AA}^6$), we have

$$B = 2 \times 20.025 \text{\AA}^3 \times 0.0169 \text{eV}/\text{\AA}^6 \times 160.2 \text{GPa}/(\text{eV}/\text{\AA}^3) = 108.5 \text{GPa}$$

This result matches with an earlier report in the literature [2]. In the elasticity theory [3], the bulk modulus B is related to the other elastic constants through

$$B = \lambda + \frac{2}{3}\mu \quad \text{for isotropic material}$$

$$B = \frac{1}{3}(C_{11} + 2C_{12}) \quad \text{for cubic material}$$

where λ and μ are Lamé's constants and C_{11} and C_{12} are cubic elastic constants. The experimental data for silicon are $C_{11} = 165.7(\text{GPa})$ and $C_{12} = 63.9(\text{GPa})$, which corresponds to a bulk modulus of $B = 98.4 \text{GPa}$. The discrepancy between the simulation and experimental results in the bulk modulus is partly because the simulation results here correspond to the ideal case of $T = 0 \text{K}$, while the experimental result is obtained at room temperature $T = 300 \text{K}$. The elastic constants generally decreases with increasing temperature. The discrepancy may also come from the fact that the potential model used here is not accurate enough, which should be expected given its empirical nature. Different parameterization of the potential model generally leads to different predictions of the elastic constants [2].

References

- [1] F. H. Stillinger and T. A. Weber, *Phys. Rev. B* **31**, 5262 (1985).
- [2] H. Balamane, T. Halicioglu, and W. A. Tiler, *Phys. Rev. B* **46**, 2250 (1992).
- [3] J. P. Hirth and J. Lothe, *Theory of Dislocations*, (Wiley, New York, 1982).